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# Catalytic reduction of $NH_4NO_3$ by NO: Effects of solid acids and implications for low temperature $DeNO_x$ processes

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**Abstract**

Ammonium nitrate is thermally stable below 250 °C and could potentially deactivate low temperature $NO_x$ reduction catalysts by blocking active sites. It is shown that NO reduces neat $NH_4NO_3$ above its 170 °C melting point, while acidic solids catalyze this reaction even at temperatures below 100 °C. $NO_2$, a product of the reduction, can dimerize and then dissociate in molten $NH_4NO_3$ to $NO^+ + NO_3^-$, and may be stabilized within the melt as either an adduct or as $HNO_2$ formed from the hydrolysis of $NO^+$ or $N_2O_4$. The other product of reduction, $NH_4NO_2$, readily decomposes at ≤100 °C to $N_2$ and $H_2O$, the desired end products of $DeNO_x$ catalysis. A mechanism for the acid catalyzed reduction of $NH_4NO_3$ by NO is proposed, with $HNO_3$ as an intermediate. These findings indicate that the use of acidic catalysts or promoters in $DeNO_x$ systems could help mitigate catalyst deactivation at low operating temperatures (<150 °C).


*Keywords:* Ammonium nitrate; Ammonium nitrite; NO; $NO_2$; $DeNO_x$

## 1. Introduction

Proposals for stricter regulatory standards for diesel exhaust emissions have spurred a flurry of research directed towards efficient low temperature (≤150–250 °C) $NO_x$ reduction [1,2]. However, $NH_4NO_3$, which is thermally stable at <250 °C [3,4] can form from $NH_3$ and $HNO_3$ that is present in $DeNO_x$ gas streams [4–9] and could potentially deactivate low temperature $DeNO_x$ catalysts [5,6]. Reactions which can remove $NH_4NO_3$ from a $DeNO_x$ stream are therefore of importance.

We have previously shown that the reduction of nitric acid or chemisorbed nitrates by NO can play an important role in low temperature $DeNO_x$ catalysis [7,8]. Based on this result it seemed plausible that $NH_4NO_3$ could also be reduced by NO to $NH_4NO_2$, thereby converting a potential catalyst poison to a desirable $DeNO_x$ intermediate: $NH_4NO_2$ readily decomposes to $N_2 + 2H_2O$ at ≥100 °C, a favorable route for reducing $NO_x$ to $N_2$ over various $DeNO_x$ catalysts [4,9].

Thermal decomposition of $NH_4NO_3$ has been studied for many years with some debate about the details of the mechanism leading to $N_2O$ formation [10–17]. $NH_4NO_3$ sublimes above 125 °C and undergoes three crystal phase changes [18] between room temperature and its melting point, 170 °C, before decomposing in the melt. If enough water is present (≥3 $H_2O$: $NH_4NO_3$), $NH_4NO_3$ dissociates to $NH_4^+$ and $NO_3^-$ ions [19]. Above ~250 °C there is a rapid exothermic decomposition to $N_2O$ and $H_2O$. This decomposition is accelerated by acids and transition metal cations [12,14,20–23], and decelerated by bases, water, and metal oxides; [12,14,20,22,24] thus changing the effective decomposition temperature. A radical-initiated explosive decomposition to $N_2$ and $H_2O$ has been reported between ~290 and 320 °C [12,14,16,25]. For these reasons we have limited our study to ≤~250 °C.

Though previous publications do not report that NO reduces $NH_4NO_3$ below its melting point of 170 °C [6–8], the present study shows that acids do catalyze this reaction below 170 °C.

## 2. Experimental

### 2.1. Materials

Na-Y Zeolite powder, >90%-100 mesh (<149 μm), nominal Si/Al = 2.5, was obtained from Aldrich (#33,444-8). BaNa-Y

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was prepared from the Na-Y zeolite stock by ion exchange in a 0.1 M $Ba(NO_3)_2$ aqueous solution at room temperature. The mixture was stirred for >24 h, then vacuum filtered with a deionized water, washed and then dried. Elemental analysis by inductively coupled plasma spectroscopy (ICP) yielded a zeolite framework composition of $Ba_{9.6}Na_{33.8}Al_{53}Si_{139}O_{384}$.

H-Y zeolite samples were prepared by baking $NH_4$-Y in air at 400 °C for >3 h. $NH_4$-Y was obtained from Zeolyst International (# CBU 712), with a nominal Si/Al ratio of 6. An actual Si/Al of 3.76 ± 0.45 was determined by ICP.

The quartz used in these studies was Davison Grade # 62, 80–200 mesh (74–177 μm) which was washed with 1 M $HNO_3$, and baked at 400 °C for 3 h. Trimethylated quartz was prepared by stirring the 74–177 μm quartz crystals in >98% chloro trimethylsilane, obtained from Lancaster Synthesis (# 200-900-5). A second sample of smaller quartz crystals, −325 mesh (<44 μm) 99.6% $SiO_2$ was used as obtained from Aldrich (#34,289-0).

$NH_4NO_3$ was obtained from Aldrich (#22,124-4, >98% purity). The water content/purity of the $NH_4NO_3$ was checked by titration with NaOH in water. A glass electrode pH probe was used during titration, with the equivalence point observed at a pH of ~10.3 as determined by the point of maximum change in pH per volume of titrant. A resolution of 0.1 pH units was required to observe the equivalence point. The quantity of NaOH required for titration corresponded to $NH_4NO_3$ samples being 102.2 ± 2.5% $NH_4NO_3$ by weight—in excess of the expected quantity of NaOH required for titration. For the three samples that were used in the titrations, values >101.3% were found. Though this is within experimental error of 100%, an "excess" of NaOH required during titration could be explained as resulting from a loss of $NH_3$ to the gas phase, leaving "excess" $HNO_3$ behind. This type of behavior has previously been observed with $NH_4NO_3(l)$ (>170 °C) and for $NH_4NO_3(s)$ at >100 °C [26,27]. In either case, there was no significant quantity of water present in the $NH_4NO_3$.

He and 2% NO in He was used as obtained from Matheson Tri-Gas.

### 2.2. Experimental setup and sample preparation

$NH_4NO_3$ was ground in a ceramic mortar and pestle prior to mixing with other solids, as it was deemed desirable that in all experiments the $NH_4NO_3$ particles have the same size. Note: very small quantities of ammonium nitrate were ground at any one time to minimize the scale of a possible decomposition reaction initiated by grinding. Optical microscopy showed that grinding $NH_4NO_3$ mixed with other powders resulted in smaller $NH_4NO_3$ crystals than grinding $NH_4NO_3$ by itself; presumably due to a ball milling effect [28,29].

In flow experiments, samples of ground $NH_4NO_3$ powder (0.2 g) were used "as is" or physically mixed with another powder (0.07 g) and placed in a quartz U-shaped reactor. The amount of $NH_4NO_3$ was in excess of the total moles of NO flowed during the duration of an experiment. Either He or NO in He was allowed to flow first through the reactor and then through a quartz cell that was sealed with NaCl windows. The gas in the flow was monitored by FTIR using a Thermo Nicolet Nexus 670 FTIR spectrometer. The IR beam passed through the chamber surrounding the IR flow-through cell, which was continuously purged with dry air to lessen background fluctuations. IR spectra were obtained at a resolution of 2 or 4 $cm^{-1}$, by averaging >8 scans taken over ~1 min. Backgrounds were obtained before an experiment by averaging ≥20 scans with a 10 cc/min He flow at atmospheric pressure. During experiments, samples were exposed to a 2% NO in He flow of 10 cc/min, with a temperature ramp of 5 °C/min from 25 to 250 °C.

Experiments in which $NH_4NO_3$ melts were exposed to $^{15}NO_2$ were performed in a quartz U-tube reactor (surrounded by a cylindrical heating jacket) which was connected to a glass bulb filled with $NO_2$. This U-tube reactor was also separated by a valve from a static FTIR cell described elsewhere [30]. The FTIR cell was evacuated, and aliquots were drawn from the gas phase of the U-reactor subsequent to cooling of the $NH_4NO_3$ melt. FTIR scans were taken at 2 or 4 $cm^{-1}$ resolution, with >4 scans averaged per spectrum. Backgrounds were obtained with ≥8 scans.

## 3. Results

### 3.1. Reduction of $NH_4NO_3$ in a flow of NO

NO was allowed to flow over $NH_4NO_3$ that was physically mixed with different solids; the effluent monitored by IR. Figs. 1 and 2 show the depletion of NO in the effluent as a function of temperature; this consumption of NO is indicative of the reduction of $NH_4NO_3$ by NO. Fig. 1 shows the depletion of NO for $NH_4NO_3$ physically mixed with solids containing varying amounts of hydroxyl groups, while Fig. 2 shows the depletion of NO for $NH_4NO_3$ physically mixed with solids of varying acidities. Production of $NO_2$, $N_2O_4$, $N_2O_3$, $HNO_3$, $H_2O$ and $N_2O$ was also observed in the effluent. For all samples, $N_2O$ production from the thermal decomposition of $NH_4NO_3$ was typically observed between 200 and 250 °C; this production is rapid between 230 and 250 °C. The $N_2O_3$ observed is expected to arise from the equilibrium with NO + $NO_2$.

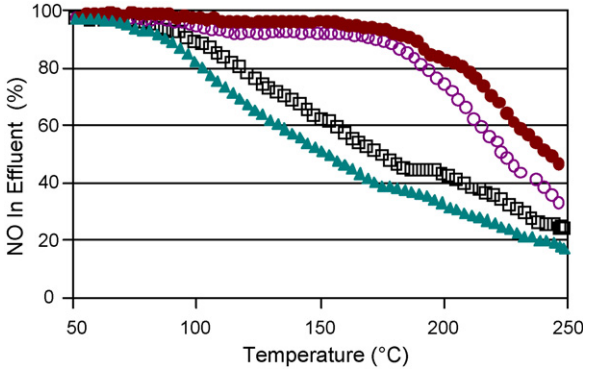



Fig. 1. NO depletion during temperature programmed reaction of neat $NH_4NO_3$ and $NH_4NO_3$ physically mixed with solids with varying amounts of surface hydroxyl groups. From top to bottom, $NH_4NO_3$—no substrate (filled circles), trimethylated 74–177 μm quartz (open circles), 74–177 μm quartz (open squares), and <44 μm quartz (filled triangles).

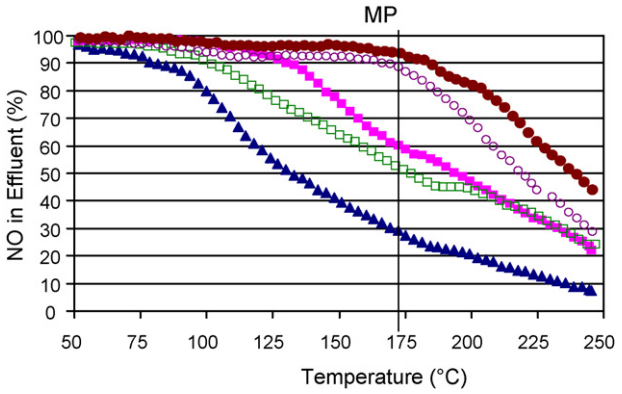



Fig. 2. NO depletion during temperature programmed reaction of neat $NH_4NO_3$ and $NH_4NO_3$ physically mixed with four different solids: $NH_4NO_3$—no substrate (filled circles), trimethylated quartz (open circles), Na-Y zeolite (filled squares), quartz (open squares), H-Y (filled triangles). Results for BaNa-Y (not shown) were qualitatively and quantitatively similar to Na-Y. For comparison the melting point of $NH_4NO_3$ (MP) is marked with a vertical line.

Concentration profiles for $NO_2$ were not stoichiometrically commensurate with NO depletion: less $NO_2$ production was observed in the effluent than the amount of NO depleted. As shown in Fig. 3, during cooling of the melt to a temperature near the 170 °C freezing point of $NH_4NO_3$, a "release" of $NO_2$ to the gas phase was observed. The amount of $NO_2$ released in such a manner varied between samples. H-Y mixtures showed the least $NO_2$ in the effluent during heating and the greatest amount of $NO_2$ released during cool down.

### 3.2. Static experiments: exchange of labeled $NO_2$

To gain insight into the ability of molten $NH_4NO_3$ to "trap" $NO_2$ and release $NO_2$ upon freezing, $NH_4NO_3$ powder was exposed to $^{15}NO_2$. Heating of this sample to 200–250 °C (above the melting point of $NH_4NO_3$) was followed by cooling. Aliquots of the gas were then analyzed to determine whether isotopic exchange occurred between $^{15}NO_2$ and molten $NH_4NO_3$. Isotopic exchange has mechanistic implications which will be discussed below.

The $^{15}NO_2/NH_4NO_3$ mole ratio was varied between 0.01 and 1.0. Based on a lack of $NO_2$ depletion in the gas phase, and the

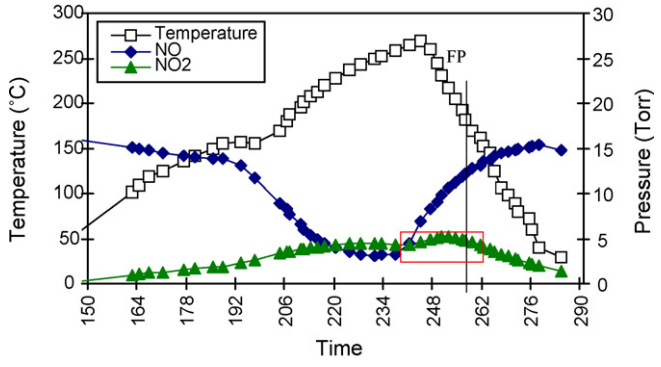



Fig. 3. $NO_2$ and NO concentrations observed in the effluent as a function of time during heating and cooling, for a flow experiment with $NH_4NO_3$ physically mixed with quartz and exposed to NO. The freezing point temperature is marked by "FP" and $NO_2$ released near the freezing point is highlighted by a box.

finite $NO_2$ isotopic exchange observed in aliquots, molten $NH_4NO_3$ only accommodates $NO_2$ as $\ll$3% of the melt. Small quantities of gas phase water and $N_2O$ were also observed after each treatment, presumably the result of the thermal decomposition of a small amount of $NH_4NO_3$.

## 4. Discussion

### 4.1. Effect of mixing with solid powders

While previous publications show that NO reduces $NH_4NO_3$ [6–8] above its melting point of 170 °C [15], the data in Figs. 1 and 2 show that when crystalline $NH_4NO_3$ is physically mixed with some solids, it is reduced by NO *even at temperatures significantly below its melting point*.

The effects of mixing micron-scale particles of $NH_4NO_3$ with micron-scale particles of other powders can be rationalized when considering the mobility of $NH_4NO_3$ at the operative temperatures. The temperature at which reaction is observed is above the Hüttig and Tamman temperatures for $NH_4NO_3$. These are the temperatures at which mobility of the solid develops at the *surface* (~1/3 of the melting point in K) or within the *bulk* (~1/2 of the melting point in K), respectively [31]. At these temperatures, the mobility of $NH_4NO_3$ allows it to spread over the surface of a solid powder. In the case of zeolites, it has previously been shown that molten $NH_4NO_3$ also enters Faujasite pores [32,33].

By coating the inner and/or outer surfaces of the solids, the $NH_4NO_3$ acquires an increased surface area and intimate contact with the solid's surface sites. The promotion of a reaction due to physically mixing $NH_4NO_3$ with solids could thus be due to either (a) the increased surface area of $NH_4NO_3$—a physical effect, or (b) interaction of $NH_4NO_3$ molecules with the terminations of the surfaces of the solids—a chemical effect.

Quartz surfaces expose weakly acidic hydroxyl groups (>90% of terminations) [34,35]. To ascertain whether the effect of solid powders on the reduction of $NH_4NO_3$ by NO is physical or chemical in nature, we compared three quartz samples: 74–177 μm quartz crystals, 74–177 μm quartz crystals passivated by trimethylsilane chloride, and <44 μm quartz crystals. The treatment of the 74–177 μm quartz crystals with trimethylsilane converts hydroxyl groups to trimethylsilanes, dramatically altering the chemical nature of the surface without changing the surface area or volume of the particles. Conversely, the <44 μm quartz crystals exposes more hydroxyl groups per unit of mass than the 74–177 μm quartz crystals due to a larger surface area. The results in Fig. 1 show a clear correlation between the quantity of hydroxyl groups and the promotion of the reduction of $NH_4NO_3$ by NO. Note that the trimethylsilated quartz has virtually no effect in promoting the reaction. These results indicate that the effect of mixing with solid powders is chemical.

As shown in Fig. 2, there is also a positive correlation between the acidity of a solid and its effect on the reduction of $NH_4NO_3$. The extent of reaction is correlated with the acidity of the solids as measured [36–38] by the heat of adsorption for $NH_3$: H–Y (~110 kJ) [39,40] >quartz (~70 kJ) [41,42] >Na-Y

(~60 kJ)[43] >trimethyl-silated quartz [44]—implying that the reduction of $NH_4NO_3$ by NO is acid catalyzed. Results for BaNa-Y (not shown in Fig. 2) were qualitatively and quantitatively similar to Na-Y. This is not unexpected since it seems reasonable that these two zeolites would have similar acidities. Note that to our knowledge the heat of adsorption for ammonia on trimethylsilane has not been measured. However, based on data in the literature the heat of adsorption for ammonia on a surface covered with methyl groups is expected to be negligible [44].

### 4.2. Mechanism

Previous studies have shown that $NH_4NO_3$ is reduced by NO above 170 °C [6–8]. $NH_4NO_3$ melts at 170 °C [15] and is in equilibrium with $HNO_3$ and $NH_3$ within the melt: [15,45]

$$NH_4NO_3 \rightleftharpoons NH_3 + HNO_3 \quad (1)$$

As was alluded to in Section 1, NO can reduce $HNO_3$ to $HNO_2$ and $NO^-_{3(ads)}$ to $NO^-_{2(ads)}$ [8] at or below 40 °C [46]. The fact that neat $NH_4NO_3$ is reduced by NO only above its melting point (where Eq. (1) is valid) suggests that $NH_4NO_3$ first dissociates to $HNO_3$, and that $HNO_3$ is subsequently reduced by NO to $HNO_2$. Similar interpretations have been presented by others [6,7,47].

The role of acid sites may then be to reversibly bind $NH_3$, thereby making $HNO_3$ available for reduction to $HNO_2$ by NO. Reversible binding of $NH_3$ by silanols has also previously been credited with increasing the efficiency of $NO_x$ reduction by $NH_3$ [48]. Subsequent to reduction, $HNO_2$ can recombine with either its geminal $NH_3$—thereby regenerating the acid site onto which the $NH_3$ molecule was adsorbed; or it can combine with the $NH_3$ of another $NH_4NO_3$ molecule, thus freeing up another $HNO_3$. The sets of steps in this sequence of reactions are then:

$$NH_4NO_3 \rightleftharpoons NH_3 + HNO_3 \quad (1)$$

$$NH_3 + A^+ \rightleftharpoons NH_3A^+ \quad (2a)$$

$$NH_4NO_3 + A^+ \rightleftharpoons NH_3A^+ + HNO_3 \quad (2b)$$

The first steps in the mechanism produce $HNO_3$ with the binding of $NH_3$ by the acid, $A^+$, through either (2b), or (1 + 2a). $HNO_3$ is a crucial intermediate that can be reduced by NO to $HNO_2$:

$$HNO_3 + NO \rightarrow HNO_2 + NO_2 \quad (3)$$

If $HNO_2$ combines with $NH_3$ from another $NH_4NO_3$ molecule through either (5a + 1) or (4):

$$HNO_2 + NH_4NO_3 \rightarrow NH_4NO_2 + HNO_3 \quad (4)$$

$$NH_4NO_3 \rightleftharpoons NH_3 + HNO_3 \quad (1)$$

$$HNO_2 + NH_3 \rightarrow NH_4NO_2 \quad (5a)$$

an $HNO_3$ is produced and this cycle returns to (3). Alternatively, if $HNO_2$ combines with an $NH_3$ molecule that was bound to an acid site

$$NH_3A^+ \rightleftharpoons NH_3 + A^+ \quad (2a)$$

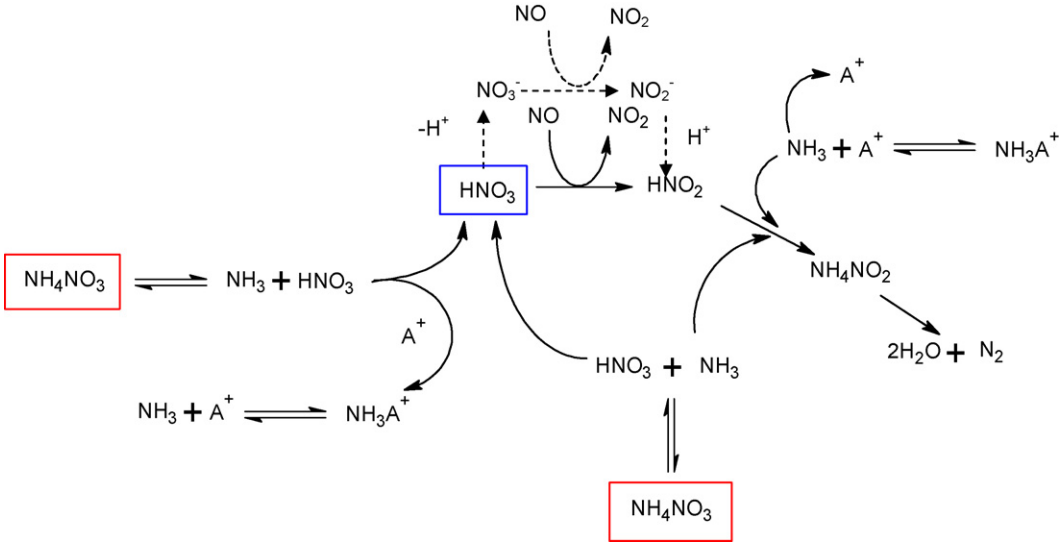
$$HNO_2 + NH_3 \rightarrow NH_4NO_2 \quad (5a)$$

$$HNO_2 + NH_3A^+ \rightarrow NH_4NO_2 + A^+ \quad (5b)$$

through either (5b) or (2a + 5a), then the acid site, $A^+$, is regenerated and the cycle involving acidic sites can restart at (2a) and (2b). Subsequent to either cycle, $NH_4NO_2$ decomposes to yield the desired products:

$$NH_4NO_2 \rightarrow N_2 + 2H_2O \quad (6)$$

The proposed mechanism is shown in Scheme 1, with the route involving chemisorbed nitrates indicated by dashed arrows and Eqs. (2b) and (5b) omitted for clarity. Note that there are two cycles. In the first of the two cycles, $HNO_2$ acquires an $NH_3$ partner from an $NH_4NO_3$ molecule (4) or (5a + 1), and an $HNO_3$ molecule is produced, returning the mechanism to (3). Alternatively, if $HNO_2$ acquires an $NH_3$ partner from an acid site (2a + 5a) or (5b), then $A^+$ is regenerated, and this cycle returns the mechanism to (1 + 2a) or (2b). In addition to the reactions listed above, on some surfaces (such as cationic sites




Scheme 1. Proposed mechanism for the acid catalyzed reduction of $NH_4NO_3$ by NO.

of Na-Y and BaNa-Y) $HNO_3$ can dissociate and form chemisorbed surface nitrates [30,49], which can then be reduced by NO [8].

This proposed mechanism allows for the first cycle, which does not require acid sites once initiated (Eqs. (1) and (3)–(5)), to continue within the bulk of the $NH_4NO_3$ melt or on other portions of the mixture's surfaces (i.e., away from the catalytic sites). Consistent with our result that the catalysis of the reduction of $NH_4NO_3$ by NO is positively correlated with a solids $NH_3$ adsorption enthalpy, the mechanism also implies that both Brønsted and Lewis acids should catalyze the reduction of $NH_4NO_3$ by NO.

### 4.3. $NO_2$ sequestration and exchange

The flow experiments on the reduction of $NH_4NO_3$ by NO show that $NO_2$ is released from the melt during cooling down at approximately the temperature of crystallization of the samples (Fig. 3). One possible explanation is that $NO_2$ dimerizes to $N_2O_4$ which then dissociates heterolytically within the $NH_4NO_3$ melt as shown below:

$$2NO_2 \rightleftharpoons N_2O_4 \quad (7)$$

$$N_2O_4 \rightleftharpoons NO^+_{(solvated)} + NO^-_{3(solvated)} \quad (8)$$

Upon freezing, the reverse reaction in Eq. (8) will be favored if the melt is a more favorable environment for ion solvation than the crystalline solid. The reactions in Eq. (8) are known to occur in highly polar environments such as Faujasite channels, [8,30,49,50] $HNO_3(l)$ [51] and other polar solutions [51]. It is also known that $NH_4NO_3$ solvates nitrate salts [52], is soluble in $HNO_3(l)$, [53] and exists in dissociative equilibrium (1) with $HNO_3(l)$ when molten [15,45]. This supports the concept that molten $NH_4NO_3$ might also solvate $NO_3^- + NO^+$ as in equation (8).

When molten $NH_4NO_3$ is exposed to $^{15}NO_2$ and cooled until it solidifies, both $^{14}NO_2$ and $^{15}NO_2$ are observed in the gas phase. Based on Eqs. (7) and (8), some of the observed $NO_2$ is due to dissociation of $N_2O_4$ (7) which is ''stored'' in the melt as $NO_3^-$ and $NO^+$ (8). The ions in the melt produced from $^{15}NO_2$ through Eqs. (7) and (8) are expected to be labeled: $^{15}NO^+$ and $^{15}NO_3^-$. Since $^{15}NO_3^-$ is expected to exchange with an unlabelled nitrate from the melt while $^{15}NO^+$ would not be expected to exchange, partial isotopic exchange would be expected, as was observed.

However, the $NH_4NO_3$ melt (*above 170 °C*) was only observed to trap $\ll$0.03 (3 mol%) $NO_2$ molecule per $NH_4NO_3$ molecule. It is unclear if the inability of $NH_4NO_3$ to retain larger quantities of $NO_2$ in these static experiments, is due to experimental conditions (e.g., extent of evacuation, lack of gas flow, lack of mixing, etc.), or other causes such as the absence of added NO. As a comparison $HNO_3(l)$ accommodates 10.2 mol% $N_2O_4$ (in equilibrium with $NO^+$ and $NO_3^-$ with the equilibrium heavily shifted toward these products) when calculated based on the total number of moles in the melt near *room temperature* [51], or 18.5 mol% $NO_2$, based on the number of $NO_2$ molecules stored.

For static cell experiments, where $NH_4NO_3(l)$ is only exposed to $NO_2$, such quantities of dissolved $NO_2$ ($\ll$3 mol%) are too low to rationalize the levels of dissolved $NO_2$ observed during flow experiments in which molten $NH_4NO_3$ is exposed to NO: in some of these latter experiments the stored $NO_2$ corresponded to >10 mol% of the melt. An alternative explanation for the apparent sequestration and subsequent release of $NO_2$ during flow experiments is that during reduction of $NH_4NO_3$ by NO an intermediate is formed from $NO_2$, and this intermediate is stabilized within the melt, released upon freezing, and decomposes to produce $NO_2$.

$HNO_2$ (HONO) is one possible candidate for an intermediate formed from $NO_2$ and stabilized within the melt until freezing. During the reduction of $NH_4NO_3$ by NO, $NO_2$ is first produced before being stored in the melt until cool down:

$$2NH_4NO_3 + 2NO \rightarrow 4H_2O + 2N_2 + 2NO_2 \quad (9)$$

If the hydrolysis of $NO^+$ can occur in the $NH_4NO_3$ melt, $HNO_2$ will be produced (11). This hydrolysis is known to occur when a salt containing $NO^+$ as a cation is dissolved in water [54] and is also believed to occur on BaNa-Y [8]. If (11) can occur in the $NH_4NO_3$ melt, then:

$$2NO_2 \rightleftharpoons NO^+ + NO_3^- \quad (10)$$

$$NO^+ + H_2O \rightleftharpoons HONO + H^+ \quad (11)$$

$$H^+ + NO_3^- \rightleftharpoons HNO_3 \quad (12)$$

$$2NO_2 + H_2O \rightleftharpoons HNO_3 + HONO \quad (13)$$

where (13) is the sum of Eqs. (10)–(12). Even if (11) is not significant in the melt, other mechanisms that produce HONO as in (13), may take place, such as through $N_2O_4 + H_2O$ [55]. Adding (9 + 13) yields:

$$2NH_4NO_3 + 2NO \rightarrow 3H_2O + 2N_2 + HNO_3 + HONO \quad (14)$$

Reaction (14) would create an excess of acids over ammonia within the melt $[HNO_3] + [HONO] > [NH_3]$. The excess $HNO_3$ in the melt created from $NO_2$ and $H_2O$ (13) would catalyze reaction 1 as described in Section 4.2. It is possible that the HONO formed is an intermediate stabilized by the melt. Upon cool down, $HNO_2$ likely cannot be stabilized within the $NH_4NO_3$ crystal, and decomposes to $NO_2$ and $H_2O$ by the reverse of (13) along with the excess $HNO_3$. Such a mechanism can explain the stored $NO_2$ observed during flow experiments. Another implication of reactions (9)–(13) is that the production of water from the reduction of $NH_4NO_3$ by NO will catalyze the reduction of $NH_4NO_3$ by NO, as a result of the production of more nitric acid within the melt. While this is one possible explanation for the storage and release of $NO_2$, other explanations are also possible, such as an $NO_2$ adduct stabilized within the melt.

### 4.4. Generality of the proposed mechanism

The mechanism proposed in Section 4.2 for the acid catalyzed reduction of $NH_4NO_3$ by NO is likely to be applicable

to other systems. Nova et al. have shown that the catalyzed reduction of $NH_4NO_3$ by NO on $VO_x$ sites proceeds by a redox mechanism above the melting point of $NH_4NO_3$, and that $WO_x$ sites do not catalyze this reaction [6,47,56,57]. A number of factors could explain why some acidic materials do not follow the mechanism proposed in Section 4.2:

(1) The material binds $HNO_3$ or $HNO_2$ too strongly.
(2) The material binds $HNO_3$ either molecularly or dissociatively in a manner where $HNO_3$ can no longer be efficiently reduced by NO.
(3) If Eq. (4) is not significant, then below 170 °C the geminal $NH_3$ must be released from the acid site for $NH_4NO_2$ to be produced, in which case acid sites that bind $NH_3$ too strongly would not follow our mechanism below 170 °C.

### 4.5. Implications for low temperature $NO_x$ abatement

The melting point of $NH_4NO_3$, ~170 °C, has been shown to be a critical temperature below which some $DeNO_x$ catalysts are known to deactivate [5,6], possibly because NO does not efficiently reduce pure $NH_4NO_3$ below 170 °C [6,7] in the absence of acid sites. The presence of acidic sites, on the catalyst or on added promoters, in low temperature $DeNO_x$ catalysts could potentially lower this critical deactivation temperature to <100 °C. These sites enhance the production of $HNO_3$, which is reduced by NO at temperatures as low as 25 °C [46]. Thus, it may be possible for acids to catalyze the reduction of $NH_4NO_3$ by NO at temperatures as low as 25 °C.

The product of the reduction of $NH_4NO_3$ by NO is $NH_4NO_2$, a desirable intermediate for low temperature $NO_x$ reduction, since it decomposes to $N_2$ and $H_2O$ at ~100 °C. In prior work, we have demonstrated that in the presence of strong acids $NH_4NO_2$ decomposes to $N_2$ and $H_2O$ at temperatures as low as 25 °C [58]. In combination, these findings suggest that incorporating acidic promoters in $DeNO_x$ catalysts, could lower the operational temperatures of $DeNO_x$ systems.

## 5. Conclusions

$NH_4NO_3$ is reduced by NO above its melting point, 170 °C. In the presence of acidic solids this reaction is catalyzed and becomes observable at temperatures as low as 70 °C. Based on the proposed mechanism, it is possible that the acid catalyzed reduction could take place at temperatures as low as 25 °C. $HNO_3$ is a crucial intermediate in the reduction of ammonium nitrate. The reduction product is $NH_4NO_2$, a desirable intermediate in low temperature $DeNO_x$ catalysis as it decomposes cleanly to $N_2$ and $H_2O$ at 100 °C, and at lower temperatures in an acidic environment. Molten $NH_4NO_3$ may stabilize $NO_3^- + NO^+$ that is formed by the heterolytic dissociative solvation of $N_2O_4$, which in turn results from the dimerization of $NO_2$ (Eqs. (7) and (8)). In addition, an intermediate formed from $NO_2$ is likely stabilized within the melt: one possibility is $HNO_2$ formed from the hydrolysis of $NO^+$ or $N_2O_4$ (10)–(13). When the melt freezes, the reverse of these reactions leads to the rapid release of $NO_2$.

These findings suggest that acidic catalysts could lower the effective temperatures for $DeNO_x$ systems by catalyzing the reduction of $NH_4NO_3$, a potential deactivator of the catalyst, to $NH_4NO_2$, a desirable intermediate in low temperature $DeNO_x$ catalysis.

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